MAGNESIUM-BASED ALLOY FOR SEMI-SOLID CASTING HAVING ELEVATED TEMPERATURE PROPERTIES

FIELD OF THE INVENTION

[001] The present invention relates to a magnesium-based alloy for semi-solid casting having elevated temperature properties. In particular, the present invention relates to a magnesium alloy casting produced using a thixotropic casting technique and a magnesium feedstock comprised of up to 20% solid fraction.

BACKGROUND OF THE INVENTION

[002] The use of magnesium alloys in automotive applications continues to grow at an unprecedented rate. Since 1990, the rate of utilisation of magnesium in automotive applications has increased some 20% on an annual basis. Magnesium has a number of attributes that make it an attractive structural material.

[003] Semi-solid processing is based on the thixotropic nature of alloys when they are cast at a given solid fraction. The shearing action of the casting process imparts low viscosity to the originally viscous semi-solid alloy giving it the fluidity needed to fill a given casting cavity.

[004] In semi-solid moulding the thixotropic feed material, or slug, is typically produced by continuous casting using electromagnetic stirring (Magnetohydrodynamic, MHD) or one of a number of production methods known in the art, for example mechanical stirring, strain induced melt activation, powder routes, granules, grain refinement/rapid cooling methods, etc.. The result of the processes is a feed material with a fine grained globular microstructure. In order for the slugs to be suitable as a basis for a thixotropic process they need to have a fine globular structure and must also be free of casting defects (such as oxides) and gas since these defects tend to carry over into the final cast product.

[005] The mechanical properties of cast alloys are strongly influenced by a variety of casting defects and artefacts, all of which reduce strength and ductility. These include entrapped gas porosity, shrinkage porosity, oxide, flux, and dross inclusions and planar defects such as cold shuts and folded oxidised surfaces. Die-castings

are especially prone to high levels of porosity due to high velocity turbulence of molten metal entering the die and oxide and flux inclusions resulting from melting and liquid metal transfer systems.

SUMMARY OF THE INVENTION

[006] The present invention addresses the above and other drawbacks by providing a magnesium-based semi-solid casting alloy having improved elevated temperature performance when cast from a semi-solid alloy slurry. The alloy comprises, in weight percent, about 3 to 7% Aluminum, about 0.5 to 3% Strontium with the balance being magnesium except for impurities commonly found in magnesium alloys. The semi-solid alloy slurry includes up to about 20% solid fraction by weight. In a particular embodiment the alloy, when cast into a casting, has an average % creep deformation at 150°C of less than or equal to about 0.04%, an average ultimate tensile strength at 150°C of at least about 174 Mpa, an average tensile yield strength at 150°C of at least about 112 Mpa, and an average % elongation at 150°C of less than or equal to about 20%.

[007] There is also provided a magnesium-based semi-solid casting alloy having improved elevated temperature performance when cast from a semi-solid alloy slurry. The alloy comprises, in weight percent, about 3 to 7% Aluminum, about 0.5 to 3% Strontium with the balance being magnesium except for impurities commonly found in magnesium alloys. The semi-solid alloy slurry includes up to about 5% solid fraction by weight. In a particular embodiment, the alloy when cast has an average % creep deformation at 150°C of less than or equal to about 0.04%, an average ultimate tensile strength at 150°C of at least about 183 Mpa, an average tensile yield strength at 150°C of at least about 116 Mpa, and an average % elongation at 150°C of less than or equal to about 17%.

[008] In a particular embodiment, the alloys have a structure including primary magnesium particles having a mean size of from about 20 to about 150 μm in a matrix of grains of magnesium having a mean size of from about 5 μm to about 20 μm reinforced with Al_4Sr intermetallic homogeneously dispersed particles having a mean size of from about 1 μm to about 10 μm.

[009] There is also provided a magnesium-based casting having improved elevated temperature performance when cast from a semi-solid alloy slurry. The slurry comprises, in weight percent, about 3 to 7% Aluminum, about 0.5 to 3% Strontium with the balance being magnesium except for impurities commonly found in magnesium alloys. The semi-solid alloy slurry includes up to about 20%, or up to about 5%, solid fraction by weight.

[010] In a particular embodiment, the above magnesium-based alloy castings are cast using a thixotropic casting process.

BRIEF DESCRIPTION OF THE DRAWINGS

[011] Figures 1A and 1B provide three magnified views using an optical microscope of the microstructure of Thixomolded® magnesium alloy with about 5% Aluminum and about 2% Strontium, referred to as AJ52x, having up to 5% solid fraction (Figure 1A) and 20% solid fraction (Figure 1B) in the reduced area of an ASTM B557 sample in accordance with an illustrative embodiment of the present invention;

[012] Figures 2A and 2B each provide two compositional contrast images derived from a backscattered electron image gathered using an electron microscope of the microstructure of Thixomolded® AJ52X alloy of up to 5% solid fraction (Figure 2A) and 20% solid fraction (Figure 2B) in the reduced area of an ASTM B557 sample in accordance with an illustrative embodiment of the present invention;

[013] Figures 3A, 3B and 3C provide a comparative magnified view using an optical microscope of the microstructure of Thixomolded® of up to 5% solid fraction (Figure 3A) and 20% solid fraction (Figure 3B) and conventionally die-cast (Figure 3C) AJ52X alloys in the reduced area of an ASTM B557 sample; and

[014] Figures 4A through 4E provide phase diagrams showing the modification to solidification range for Mg-Al alloys having various Strontium contents: without Strontium (figure 4A), with 0.05% Strontium added (figure 4B), with 1% Strontium added (figure 4C), with 2% Strontium added (figure 4D), and with 3% Strontium added (figure 4E).

DETAILED DESCRIPTION OF THE ILLUSTRATIVE EMBODIMENTS

[015] An understanding of the present invention begins with an understanding of the characteristics of thixotropic metal alloys and of the semi-solid casting process that can be used to cast such alloys. A thixotropic metal alloy is a multi-component (typically bi-metal or tri-metal) alloy capable of forming a casting that has extreme ductility in comparison to traditional diecastings, which are very brittle. Another major advantage of thixotropic alloys, and one having particular applicability to the present invention, is that they can be cast or otherwise formed in a semi-solid phase. This is because one metal of the alloy, forming the minority of the alloy by volume, melts before the other metal(s) forming a majority of the alloy's volume. As a result, a thixotropic alloy ingot can be cast in a semi-solid phase in which it retains its shape and can be handled but is very soft.

[016] In its semi-solid phase, a thixotropic alloy exhibits high liquid-flow characteristics when it is subject to shear. As a result, a thixotropic alloy shot fills a mould well during a casting process, and typically much better than conventional molten liquid material, as the shot enters the mould as a wave front rather than as a spray and therefore does not trap any gas. The resultant casting is pore-free. Casting of thixotropic alloys therefore can yield a material with the same qualities as a forging.

[017] Elimination of defects and reductions of porosity leads to improvements in the quality and performance of the magnesium alloy castings. In addition to elimination of defects, control of the structure of cast metals, including the size, distribution, and location of precipitates, the size and morphology of crystalline phases, the amount and location of porosity and the final grain size of the material have a direct impact on the resulting properties.

[018] One method of semi-solid casting of thixotropic alloys is Thixomolding®, a metallurgical process where metals and metal matrix composites are heated and stirred in the solid plus liquid phase region then injected into a mould or die at lower temperatures. Thixomolding® is basically a metal casting variant of plastic injection moulding combined with semi-solid casting. The process allows for the production of cast parts having improved material characteristics and allows for the casting of

shapes which are in many cases unobtainable using other currently available processes.

[019] Thixomolding® as described in US Patents No. 4,694,881 and 4,694,882 is based on the principle that magnesium, aluminum and zinc alloys become semi-solid at temperatures between the *liquidius* and the *solidius*. Mechanical shearing of the semi-solid metal generates a thixotropic structure that allows these materials to be moulded utilising a process similar to plastic injection moulding while eliminating the environmental impacts of diecasting. Unlike diecasting, the process does not require the handling of molten metals in separate melting and transfer systems.

[020] Thixomolding® produces parts from a single step process involving high-speed injection moulding of semi-solid thixotropic alloys. An apparatus for carrying out Thixomolding® is described in US Patent No.5,996,679. Feedstock chips/pellets are fed from a storage hopper into a heated shot sleeve containing a reciprocating screw feeder. The thixotropic magnesium alloy is conveyed through a controlled multi-temperature heating zone by a screw feeder while being heated to around 600°C, which is just enough to place the alloy somewhere between a liquid and a solid and thereby forming a slurry. The slurry is conveyed into a shot accumulator via a non-return valve, all the while under a blanket of inert argon gas.

[021] Unlike other semi-solid processes, a wide range of fraction solids can be used as there is no slug which has to be mechanically handled. After reaching the desired fraction solid the slurry is injected into the mould cavity under high pressure. The higher viscosity when compared to molten metal diecasting allows the flow front to remain more laminar as the die is filled thereby minimising entrapped gas porosity. Also, as the alloy is partially solidified, there is less shrinkage during solidification.

[022] An alloy was prepared, hereinafter designated as AJ52x, and tests carried out to estimate the performance of AJ52x under two moulding conditions. Geometry of the samples complied with ASTM 557 standard, i.e. 6.35 mm (1/4 inch) diameter, 8 inch long samples. Two different solid fractions were used:

- 0 to 5% of solid fraction
- 20% of solid fraction

[023] The chemical composition of the magnesium alloy tested is tabled following:

Table 1

Elements	(Weight in %)
Al	5.24
Be	0.0005
Cu	0.0010
Fe	0.0037
Mn	0.43
Ni	0.0005
Si	0.008
Sr	1.92
Zn	0.041
Mg	Remainder

[024] Mechanical tests and microstructural characterisation were performed for each solid fraction. The results obtained were compared with results obtained from diecast samples of a same ASTM geometry.

[025] Table 2 summarises tensile tests results for various moulding conditions. Geometry of the sample is similar in all cases. It can be observed, when compared with properties of diecast samples, the tensile properties are significantly better for the semi-solid cast samples using up to 5% of solid fraction. Additionally, samples with 20% of solid fraction show some improvement at temperature greater than 150°C for Ultimate Tensile Strength (UTS) and elongation, when compared with diecast samples.

[026] The minimum improvement of tensile properties using semi-solid process was calculated using a correction to reduce the effects of statistical dispersion and to better judge the improvement of tensile properties due to the semi-solid process. The improvement is calculated using the differences between the average plus one standard deviation for the diecast result and the average minus one standard deviation for the semi-solid conditions. Using this methodology, the range of improvement is, depending on temperature and solid fraction, from:

- 2 to 15 % improvement over diecast in Ultimate Tensile Strength (UTS);

- 0 to 5 % improvement over diecast in Yield Strength (YS); and
- 0 to 40% improvement over diecast in elongation.

Table 2

Casting conditions and samples geometry	AJ52x Thixomolded® up to 5% Solid fraction 6.35 mm (1/4 inch) diameter samples			AJ52x Thixomolded® 20% Solid fraction 6.35 mm (1/4 inch) diameter samples			AJ52x Diecast 6.35 mm (1/4 inch) diameter samples		
Value and (Standard dev.)	(MPa) UTS	(MPa) YS	(%) Elong	(MPa) UTS	(MPa) YS	(%) Elong	(MPa) UTS	(MPa) YS	(%) Elong
20°C	244 (6)	144 (3)	8 (1)	213 (11)	132 (5)	4 (1)	211 (22)	136 (6)	6 (2)
125°C	211 (8)	126 (1)	16 (1)	198 (1)	118 (4)	12 (1)	N/A	N/A	N/A
150°C	183 (2)	116 (1)	17 (2)	174 (1)	112 (3)	20 (2)	158 (9)	110 (4)	13 (5)
175°C	164 (1)	111 (1)	17 (1)	157 (2)	108 (5)	20 (2)	138 (4)	101 (4)	17 (9)

[027] Note that Table 2 provides median values for test samples fabricated from the AJ52x alloy with about 5% Aluminum and about 2% Strontium. It would be expected that some improvement in the above median values for a given solid fraction (5% or 20%) could be achieved by varying the amounts of Aluminum and Strontium within the 3% to 7% range for Aluminum and 0.5% to 3% Strontium.

[028] As summarised in Table 3, the tensile creep elongation at 50 MPa, 150°C and 200hrs were not different for diecast or semi-solid cast (Thixomolded®) AJ52x test samples. It should be noted that aluminum A380 has tensile creep elongation of 0.08% and AZ91D a non high temperature creep resistant alloy has 2.7% under the same test conditions. Semi-solid cast AJ52x samples show superior creep resistance than aluminum A380, for the two solid fractions investigated, under the tested conditions.

Table 3

All y	AJ52x	AJ52x	AJ52x	Al 380	AZ91D
Casting conditions	Thixomolded® 0 to 5% Solid fraction	Thixomolded® 20% Solid fraction	Diecast	Diecast	
Sample geometry	6.35 mm (1/4 inch) diameter samples	6.35 mm (1/4 inch) diameter samples	6.35 mm (1/4 inch) diameter samples	6.35 mm (1/4 inch) diameter samples	6.35 mm (1/4 inch) diameter samples
200 Hrs Creep (%) 50 Mpa 150°C	0.04	0.04	0.04	0.08	2.70

[029] As summarised in Table 4, the creep rate for AJ52x is reduced by two to three orders of magnitude when compare with non creep resistant alloy AZ91D and the low creep resistant magnesium alloy AS41B. Note that, for AZ91D and AS41B, the test results are in part derived from documents in the public domain. The alloys tested were subject to various stresses and temperatures. Generally, at a given stress, creep rate increases with temperature, and at a given temperature, creep rate increases with stress. AJ52x with 5% and 20% at 50 MPa/150°C of solid fraction show lower creep rate than AZ91D at 50 MPa/125°C, 50 MPa/150°C. AJ52x with 5% and 20% at 50 MPa/150°C of solid fraction show lower creep rate than AS41 at 70 MPa/125°C, 70 MPa/150°C. As AZ91D, AJ52x shows lower creep rate for high solid fraction.

Table 4

Alloy	Solid Fraction (%)	Temp (°C)	Stress (MPa)	Creep Rate (in/in/sec)
AZ91D (1,3)	4	125	50	1.12×10^{-8}
AZ91D (1,3)	39	125	50	7.5×10^{-9}
AZ91D (2,3)	<5	125	50	1.0×10^{-8}
AZ91D (3)	Diecast	125	50	1.35×10^{-8}
AZ91D	Diecast	150	50	4.4×10^{-7}
AS41B (2,3)	<5	125	50	3×10^{-9}
AS41B (2,3)	<5	125	70	$1. \times 10^{-6}$
AS41B (2,3)	<5	150	70	8.1×10^{-6}
AJ52x	5	150	50	2.4×10^{-10}
AJ52x	20	150	50	1.5×10^{-10}
AJ52x	Diecast	150	50	7.4×10^{-11}

[030] Cross-sections were prepared from the semi-solid cast samples, in the reduced section, close to the grip areas. The samples were examined using optical and scanning electron microscopes. Figures 1A and 1B compare both the up to 5% and 20% semi-solid casting fraction conditions. At low magnification, the primary particles can clearly be seen with a white colour over a dark background. As expected, the volume fraction of primary particles is close to the solid fraction conditions targeted for semi-solid casting.

[031] The primary particle distribution in the lower solid fraction condition is quite uniform and no clustering of particles was observed. For the higher solid fraction, the particle distribution is relatively uniform. However, a 10 microns particle-free skin can be observed. The density of primary particles is apparently larger in the central portion of the sample.

[032] The primary particles are relatively free of any second phase particles (visible in the larger magnifications in Figure 1A and 1B). In some primary particles, MnAl and SrAl phases can be observed (see Figures 2A and 2B). Surrounding the primary particles, the liquid-Mg structure solidified with a relatively small microstructure. The "secondary" microstructure seems to be slightly coarser in the 0-5% solid fraction condition when compared to 20% solid fraction.

[033] The phase make-up in the secondary structure is typical of a high-Al AJ52x alloys where the eutectic Al_4Sr phase can be observed and Al-coring can also be observed at the Mg grain boundary (see Figures 2A and 2B). The volume fraction of Al_4Sr phase in the secondary structure appears larger in the 20% solid fraction condition than in 0-5% condition. During the formation of the primary particles, Al and Sr will segregate in the liquid leading to an enrichment of the secondary structure. The Al-coring appears to be similar for both conditions. The $Mg_{17}Al_{12}$ phase, which is detrimental to the creep resistance, was not observed in samples from both fraction conditions.

[034] The microstructure is similar to the one observed in diecast samples (see Figures 3A, 3B and 3C). However, the microstructure of diecast sample is less uniform (when compared to the secondary structure) than the semi-solid moulded

samples. The diecast structure shows very fine grains with some large fully develop dentritic grains.

[035] Referring to Figures 4A through 4E the semi-solid moulded and diecast microstructures were compared using x-ray diffraction which is sensitive to phase make-up and the results graphed. The three samples (5% solid fraction, 20% solid fraction, diecast) showed a similar phase make-up where Al_4Sr peaks were clearly seen. The $Al_3Mg_{13}Sr$ phase, which is observed in low-Al/high-Sr AJ52x, was not detected in the two semi-solid samples.

[036] Still referring to Figures 4a through 4E, the microstructure developed by the thixotropic semi-solid casting, with 0-5% solid fraction, is more uniform than the microstructure of a casting fabricated using diecasting. The lower tensile properties observed with the 20% solid fraction condition are likely related to the lack of precipitates in the primary particles and an improvement may potentially be obtained by lowering the size of the primary particles.

[037] The phase make-up is similar for both semi-solid cast and diecast samples. The tensile strength values obtained for the semi-solid cast samples of an AJ52x alloy with 0 to 5% of solid fraction are, at room temperature, similar to that of a die-cast AZ91D alloy.

[038] The semi-solid zone defined between the solidius and the liquidius lines of Figures 4A to 4E is modified by the addition of Strontium. When no Strontium is added to the alloy (Figure 4A), the solidification range, which is illustrated by the distance between the liquidius and solidius lines, increases with an increase in the percentage of Aluminum added.

[039] Referring now to Figure 4B, when 0.5% Strontium is added, a saddle point appears at about 5% Aluminum in the liquidius line. The solidification range is significantly increased for an alloy containing less than 7% Aluminum when compared with the non-Strontium containing alloy of Figure 4A. By increasing the semi-solid zone of the alloy, the temperature range can be suitably improved thereby allowing for the use of the alloy in a slurry which can be injected inside a mould using a semi-solid process such as Thixomolding®.

[040] When additional Strontium is added to 1% (Figure 4C), 2% (Figure 4D) and 3% (Figure 4E), the saddle point in liquidius does not move significantly and the solidification characteristics remain similar for magnesium alloys having from 0.5 to 3% Strontium and 3 to 7% Aluminum.

[041] The phase diagrams (Figures 4B to 4E) thus predict the formation of magnesium alloys containing Al_4Sr, which is a suitable phase for alloy having improve elevated temperature properties.

[042] Although the present invention has been described hereinabove by way of an illustrative embodiment thereof, this embodiment can be modified at will, within the scope of the present invention, without departing from the spirit and nature of the subject of the present invention.